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Compression behaviour of single wall carbon nanotube under high pressure

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In the present investigation, we have analyzed the pressure dependence of compressional behaviour of nanotube bundle and individual ne bundle of single wall carbon nanotube For this purpose, we have used usual Tait's Equation of State to predict the change in unit cell function of pressure We have also predicted the variation of isothermal bulk modulus and specific heat with pressure for nanotube The ed from usual Tait's Equation of State are found in good agreement with the available experimental data It is concluded that the individual ube is less compressible than the bundle of carbon nanotube

Nanomaterial, specific heat, volume compression

61 46 Fg, 62 25 +g, 64 30 +t

Introduction

e the first report of carbon nanotubes by Iijima [1], carbon otubes have got a lot of attention because of their unique tronic and mechanical properties As a one dimensional cture, carbon nanotubes can be thought of as one sheet or ltiple sheets of graphene rolled into a cylinder They have gle or multiple layers of carbon atoms in the tube thickness on, called single-walled carbon nanotubes (SWCNTs) or lti-walled carbon nanotubes (MWCNTs), respectively cording to different chiral angles, SWCNTs can be classified zigzag ($\theta = 0^0$), armchair ($\theta = 30^0$) and chiral tubes ($0 < \theta < 30^0$) [2]

SWCNT bundles typically consist of several nested tubes, h like a graphene sheet bent into the cylindrical form, with an erall diameter of a few nanometers Due to the van der Waals raction, each SWCNTs tends to form close packed bundles The most important property of carbon nanotubes (CN's) is ir elastic response to the external force or stress [4,5]. The stic properties of nanotubes are highly anisotropic In the rection along the tube axis, the material is extremely rigid [6] th a Young's moduli in the range of terapascal [7] and along the radial direction, carbon nanotubes are extraordinarily flexible and elastic However, their circular sections can be deformed and even collapsed [8,9] as induced by the external forces [10],local bents or defects [11], or by van der Waals forces [12] The tubes are most easily distorted perpendicular to their axis, and any mechanical failure occurs most easily between tubes

The Young's modulus and Poisson's ratio of nanotube which are the most interesting elastic properties have been studied by the previous workers [13-17] The hardness as one of the most important parameters characterizing the mechanical properties of SWCNTs has been intensively studied during last decade [14,18] In the present work, we have investigated the mechanical properties especially the bulk modulus and the compression (V/Vo) of nanotube bundles using the usual Tait's equation of state (EOS) We have then compared our calculated results with the experimental values and also with those results obtained for graphite During last decade, the Tait's equation has been widely used in most of the bulk materials [19-21], however, this equation has not been used so far to analyze the compression behaviour of nanomaterials In our present work, we have also calculated the variation of specific heat and isothermal bulk modulus with pressure for nanotube.

Experimental values of bulk modulus and its first derivative of nanotube bundle (K_0 = 37GPa, K_0^1 =11) and individual tube within the bundle (K_0 = 230GPa, K_0^1 = 4 5) have been taken from Ref [22] For this purpose, Reich and Thomson [22] have used the first principle method (*i e ab-initio* method) and calculations are performed by using local-density approximation of density-functional theory to calculate these values From X- ray diffraction, the experimental values of bulk modulus and its first derivative for graphite are measured by Hanfland *et al* [23] which are reported as K_0 = 33 8GPa and K_0^1 = 8 9, respectively

2. Method of analysis

Investigation of compressional behaviour of bulk solids has been the subject of great interest [19-21] for its importance in understanding the microscopic behaviour of bulk solids in physics and geophysics The usual Tait equation of state has been found most useful nonlinear relation to explain thermoelastic properties of different class of solids and liquids [24] This equation of state has now been applied to analyze the compression of unit cell volume and the rigidity of nanomaterials under pressure in the present study The usual Tait equation of state is obtained by assuming the fact that the product of the thermal expansion coefficient (α) and the bulk modulus (K_T) is constant under the effect of pressure [25] *i e*

$$\alpha K = \text{constant} \tag{1}$$

Differentiation of eq (1) with respect to volume at constant temperature, gives

$$\alpha\left(dK/dV\right)_T + K\left(d\alpha/dV\right)_T = 0 \tag{2}$$

Anderson-Gruneisen parameter is defined as

$$\delta_T = V/\alpha\left(d\alpha/dV\right)_T, \tag{3}$$

where δ_T is Anderson-Gruneisen parameter at constant temperature

From eqs (2) and (3),we get

$$\delta_T = V/\alpha\left(d\alpha/dV\right)_T = -V/K\left(dK/dV\right)_T \tag{4}$$

Assuming δ_T to be independent of V,

$$\delta_T = \left(dK/dP\right)_T = K_0^1 \tag{5}$$

Anderson-Gruneisen parameter δ_T and $\eta = V/V_0$ (where V_0 is the initial volume) are related by the following relation [26]

$$\left(\delta_T + 1\right)/\eta = A, \tag{6}$$

where, A is a constant for a given solid. In view of eq (6) eq (3) can be written as

$$dK/K = \left[-A/V_0 + 1/V\right]dV$$

Integrating above equation, we get

$$K/K_0 = V/V_0 \exp A\left[1 - V/V_0\right],$$

where $K = -V\left(dP/dV\right)_T$

In view of eq (9), eq (8) is written as

$$K/K_0 \exp A\left[1 - V/V_0\right]dV = -dP$$

The integration of eq (10)gives

$$P = K_0/A\left[\exp A\left(1 - V/V_0\right) - 1\right]$$

Here, K_0 is the bulk modulus at the zero pressure and the constant A is determined from the initial conditions, *i e* $V = V_0$, $A = \delta_T^0 + 1$

On substitution of A in eq (11) and taking the natural log we get the following final form of usual Tait equation of state

$$\left[V(P,T_0)\right]/\left[V(0,T_0)\right] = 1 - 1/K_0^1 + 1$$

$$\times \ln\ 1 + \left(K_0^1 + 1\right)/K_0$$

where $V(P, T_0)$ is the volume of the solid at pressure required to compress it, keeping the temperature constant V_0 is the initial volume at P = 0 at room temperatureT_0 K_0 and K_0^1 are the isothermal bulk modulus and its first pressure derivative at $T = T_0$

The beauty of this equation of state is that it requires the number of input parameters and provides a simple and straightforward approach to predict the relative compression in solids at high pressure. To test the validity of this equation of state for nanomaterials, (as in bulk materials), we have, therefore employed Tait's equation of state to predict the compression behaviour of carbon nanotubes and graphite

Within the framework of UTE, (Usual Tait's equation) the expression for the isothermal bulk modulus can be written as [24,27]

$$K_T/K_0 = V/V_0\left\{1+\left[\left(K_0^1+1\right)/K_0\right]P\right\}. \quad (13)$$

Further, the calculation for the specific heat of nanotubes, we have followed the procedure recently provided by Saxena *et al* [28] They have provided an empirical relation for the specific heat of nanotubes as the function of radius which reads as

$$C_v = C_{V0} + A_V e^{-(R/R^0)}, \quad (14)$$

where C_{V0} A_V and R_0 are the constants such that for zigzag nanotube i e (10,0), $C_{V0} = -3600$J/Kg-K^0, $A_V = -3200$J/Kg-K^0 and $R = 1.5$Å

R is the tube radius In view of eq (12), the ratio of R/R_0 in eq (14) can be replaced in terms of the cylindrical volume of the tube as the function of pressure Eq (14) thus becomes

$$C_v = C_{V0} + A_V \exp\left[-\sqrt{1-\frac{1}{\left(K_0^1+1\right)}\ln\left\{1+\left(\left(K_0^1+1\right)/K_0\right)P\right\}}\right] \quad (15)$$

Results and discussion

In the present study, we have calculated the values of (V/V_0), specific heat (C_v) by making use of eqs (12), (13) and (15), respectively It may be noted from the Table 1 that the values of relative compression in individual as well as nanotube bundle calculated from usual Tait's equation (12) represent closer agreement with the *ab-initio* calculations and also with the experimental data [29] A graphical presentation between the present calculated values, *ab-initio* calculations and experimental values has also been shown in Figures 1 and 2 for the sake of comparison It is found in the present study that the nanotube bundle is more compressible at high pressure as compared to the individual tube within the bundle.The variation of isothermal bulk modulus (K_T) with pressure for nanotube bundle and individual tube within the bundle are shown in Figures 3 and 4 From the Figures 3 and 4, it is clear that the isothermal bulk modulus increases

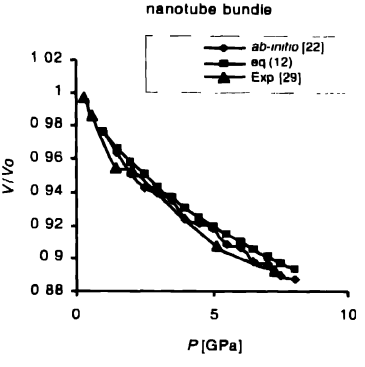

Figure 1 Shows the variation of relative compression (V/V_0) with pressure for nanotube bundle

Table 1 Relative compression (V/Vo), specific heat (C_v) and isothermal bulk modulus (K_T) for (10,0) carbon nanotube

P(GPa)	V/V_0(Cal) bundle	V/V_0 (*ab-initio*) bundle	V/V_0(Cal)	V/V_0 (*ab-initio*) individual	C_v bundle	K_T bundle	K_T individual
	0 9766	0 9769	0 9957	0 9944	412 717	47 853	234 487
	0 9670	0 9638	0 9936	0 9925	418 494	53 183	236 725
	0 9583	0 9513	0 9915	0 9900	423 819	58 459	238 952
	0 9505	0 9425	0 9894	0 9888	428 635	63 685	241 166
	0 9434	0 9400	0 9874	0 9863	433 040	68 866	243 394
	0 9368	0 9350	0 9854	0 9838	437 157	74 007	245 611
	0 9307	0 9238	0 9834	0 9825	440 999	79 109	247 817
	0 9250	0 9213	0 9814	0 9800	444 621	84 176	250 012
	0 9197	0 9188	0 9795	0 9781	447 999	89 209	252 221
	0 9147	0 9088	0 9775	0 9765	451 205	94 212	254 394
	0 9100	0 9063	0 9756	0 9750	454 237	99 186	256 583
	0 9055	0 8981	0 9737	0 9725	457 150	104 132	258 761
	0 9013	0 8963	0 9719	0 9700	459 886	109 053	260 955
	0 8972	0 8900	0 9700	0 9688	462 574	113 948	263 112
	0 8934	0 8875	0 9682	0 9663	465.048	118 820	265 287

with pressure and the compression decreases with pressure in these nanotubes and thus, follows the same trend as in the bulk solids The variation of bulk modulus with pressure could not be compared with the experimental values since the experimental data on bulk modulus of nanotubes under study are not available However, our calculated values of bulk modulus may stimulate the experimental investigations in future

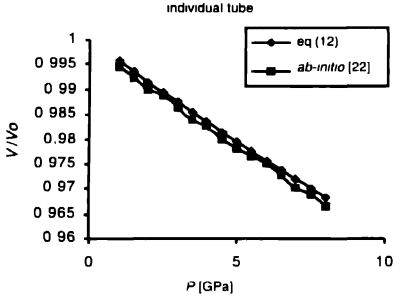

Figure 2 Shows the variation of relative compression (V/V_0) with pressure for individual tube within the bundle

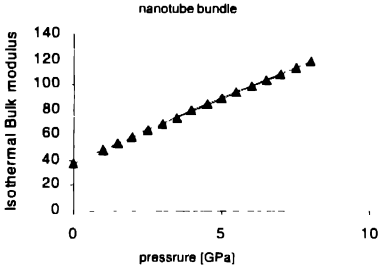

Figure 3 Shows the variation of isothermal bulk modulus (B_T) with pressure for nanotube bundle

Table 2. Relative compression (V/V_0) with pressure for graphite

P(GPa)	V/V_0(Exp)	V/V_0(Cal)
0	1	1
2 0870	0 9618	0 9518
3	–	0 9363
3 0434	0 9507	0 9356
4 8696	0 9204	0 9105
6 9565	0 8961	0 8878
8 3478	0 8809	0 8751
9 0434	0 8737	0 8693
10 434	0 8665	0 8586
11 913	0 8566	0 8483
13 913	0 8500	0 8359

In Table 2, we have reported the values of the compressi in graphite calculated by using the usual Tait's equation of A graphical presentation between the present calculated V_0 and experimental values has been shown in Figure 5 It is fou in the present study that the graphite is more compressible th the nanotube bundle which is formed by rolling graphene sh To check this nature of compressibility in nanomaterials an graphite which is treated as bulk material, we have, reported values of compression in individual nanotube, bundle o nanotube and graphite at a common pressure (30Pa) in Tab 1 and 2

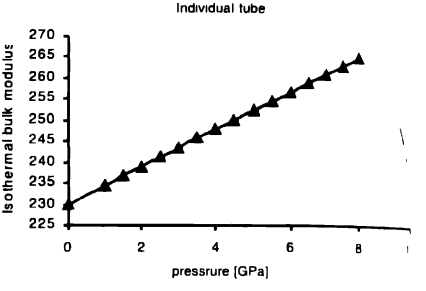

Figure 4 Shows the variation of isothermal bulk modulus(B_T) with pressu for individual tube

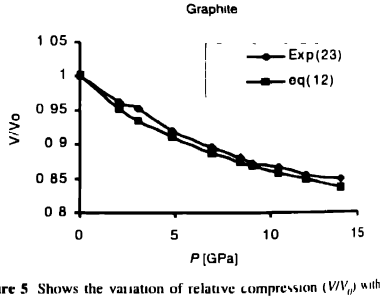

Figure 5 Shows the variation of relative compression (V/V_0) with for graphite

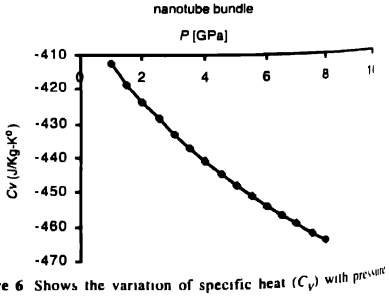

Figure 6 Shows the variation of specific heat (C_V) with pressure nanotube bundle

The pressure dependence of specific heat (C_v) for nanotube
ile has been calculated by making use of an empirical
ion[15]. It is evident from Figure 6 that the specific heat
eases with pressure in nanotube bundle. This may be
uted the fact that the nanomaterials get more and more
with pressure. On the basis of overall descriptions, it may
be concluded that the usual Tait equation of state is equally
ble of explaining the mechanical properties of nanomaterials
the bulk materials.

wledgment

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